Photochemically Induced Fluorescence Control with Intermolecular Energy Transfer from a Fluorescent Dye to a Photochromic Diarylethene in a Polymer Film

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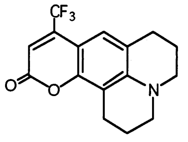
Control of chemical and physical properties of photochromic compounds by photoirradiation has been widely studied because of their potential application of reversible optical data storage and memory devices.[1−4] Changes in absorption spectra of photochromic compounds, such as diarylethenes,[2] fulgides,[3] and spiropyrans,[4] are by far the most common detection methods used today. Developments in photochromic compounds with thermal irreversibility and fatigue resistance have enhanced the possibility for practical use. However, this system has a problem that the readout process brings about partial erasure of the stored information.

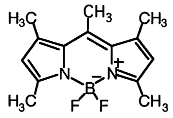
To realize a nondestructive readout system, we can use several methods including changes in refractive index,[5−8] luminescence,[9−14] and optical rotation.[15] Among them, changes in luminescence are one of the most attractive candidates for the nondestructive system because of its excellent properties such as high sensitivity, high resolution, and high contrast. The system where luminescence is reversibly controlled can be effectively applied to polymer films because polymer films provide several advantages in processability and reasonable cost performance.

An effective approach to make luminescence patterns on a polymer film is obtained when both a photochromic compound and a fluorescent dye are molecularly dispersed in the polymer film where fluorescence intensity of the fluorescent dye can be reversibly controlled by photoisomerization of the photochromic compound. In this system the fluorescent dye fluoresces when there is no interaction between its excited state and the ground state of the photochromic compound but cannot fluoresce when there is some interaction such as energy transfer or exciplex formation leading to fluorescence quenching between the excited state of the fluorescent dye and a photoisomerized state of the photochromic compound. By choosing a suitable combination of a fluorescent dye and a photochromic compound, complete on−off of fluorescence can be realized.

In the present study, we demonstrate reversible fluorescence control with complete on−off of a polymer film molecularly doped with both fluorescent and photochromic dyes. The fluorescence was effectively quenched by energy transfer from a fluorescent dye to a colored form of a photochromic compound dispersed in a polymer film. The switching characteristics are well controlled by changing the concentration of the photochromic compound, and the critical concentration of the photochromic compound for static quenching was estimated experimentally.

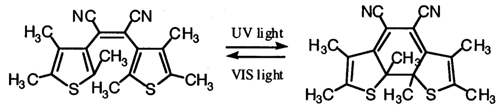
Materials for the experiments are commercially available. We used poly(methyl methacrylate) (PMMA) as a polymer matrix, *cis*-l,2-dicyano-l,2-bis(2,4,5-trimethyl-3-thienyl)ethane (CMTE) as a photochromic compound, and 2,3,5,6-1*H*,4*H*-tetrahydro-8-trifluoromethylquinolizino[9,9*a*,1-*gh*]coumarin (C540A) or 4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3*a*,4*a*-diaza-*s*-indacene (PM546) as a fluorescent dye. The chemical structures of the fluorescent dyes are shown below.


C540A


PM546

PMMA was used after reprecipitation from methanol. Films for absorption and fluorescence spectrum measurements were prepared on the quartz substrates by a spin-coating method from about l wt % solutions in toluene.

The photoisomerization of CMTE[2e] is shown in eq 1 and was carried out by using a He−Cd laser (KIMMON L124) with a wavelength at 325 nm or a 450 W high-pressure mercury lamp with KL30 filter for the ring-closing reaction and using the same mercury lamp with VY50 filter for the ring-opening backward reaction.



CMTE (open form) CMTE (closed form) (1)

The absorption spectra of CMTE before and after photoirradiation were measured in a PMMA film containing 20.5 wt % of CMTE. The changes in absorption spectra of CMTE in the PMMA film during photoirradiation are shown in Figure 1. During UV irradiation the transparent open form of CMTE photoisomerizes to the colored closed form with the increase in absorption peak at 518 nm. After 60 min, the photostationary state was reached, and the backward reaction from the colored closed form to the open form was accomplished by photoirradiation in a visible wavelength region.

The absorption and fluorescence spectra of the fluorescent dyes were measured in PMMA films as also shown in Figure 1. Absorption peaks of C540A and PM546 in PMMA films were at 418 and 496 nm, respectively. Fluorescence peaks of C540A and PM546 in PMMA films were at 489 and 510 nm, respectively, which are close to the absorption peak of the closed form of CMTE (518 nm). Since a large fluorescence and absorption spectral overlap between the fluorescent dye and the closed form of CMTE is essential for effective singlet excitation energy transfer from the fluorescent dye to the closed form, the combination of C540A or PM546 with CMTE is desirable for complete on−off of fluorescence in a polymer matrix.

Fluorescence spectra of a PMMA film containing CMTE and a fluorescent dye, C540A or PM546, were measured before and after photochromic reaction, where the concentration of the fluorescent dye in the PMMA

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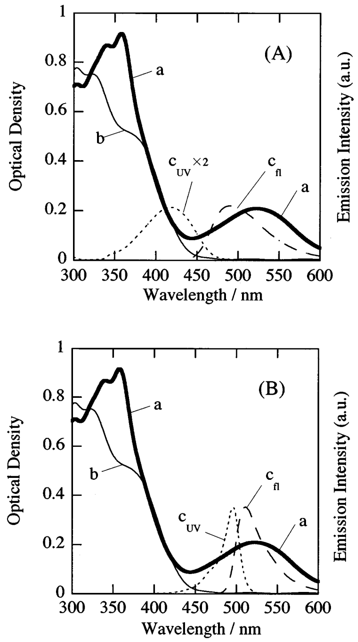

Figure 1. Absorption spectra of CMTE (20.5 wt %) in the PMMA film before (b, fine line) and after (a, bold line) photoisomerization and absorption (c_{UV}, dotted line) and fluorescence (c_{fl}, broken line) spectra of C540A (A) and PM546 (B) in PMMA films.

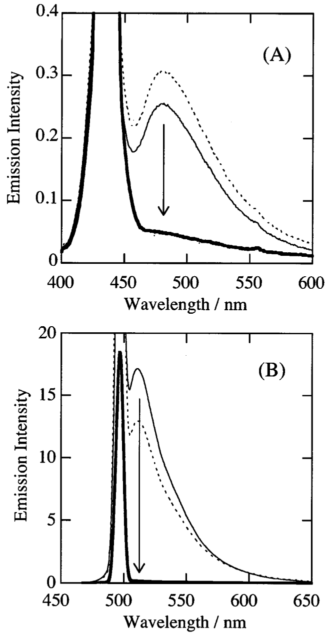

Figure 2. Fluorescence spectra of PMMA films containing 1.70 wt % of C540A and 10.2 wt % of CMTE (A) and 0.25 wt % of PM546 and 9.97 wt % of CMTE (B) before photoirradiation (fine line), after UV irradiation (bold line), and after visible light irradiation (dotted line). Fluorescence excitation wavelength: 435 nm for C540A and 496 nm for PM546.

Table 1. Fluorescence Intensities at 500 nm (C540A) and 550 nm (PM546) and Their Ratios before and after Photoisomerization of CMTE in PMMA Films Containing C540A or PM546 with CMTE

	CMTE concn [wt %]	I_b[a]	I_a[b]	I_b/I_a
C540A	0	9.2	9.2	1.0
	2.07	0.76	0.30	2.5
	4.85	0.36	0.079	4.6
	10.2	0.21	0.041	5.1
	19.1	0.10	0.031	3.3
PM546	0	23.4	23.4	1.0
	2.06	19.0	3.0	6.3
	4.86	7.5	0.53	14
	9.97	5.4	0.087	62
	19.6	1.9	0.0030	633

[a] Fluorescence intensity before UV irradiation. [b] Fluorescence intensity after UV irradiation.

film was fixed and that of CMTE was changed. Spectral changes of the PMMA film containing 1.70 wt % of C540A and 10.2 wt % of CMTE during photoirradiation are shown in Figure 2A. By UV irradiation, the fluorescence of C540A excited at 435 nm was quenched accompanied by photoisomerization of CMTE from the open form to closed one and by photoirradiation around 500 nm on the film; the fluorescence of C540A reappeared accompanied by the backward photoisomerization of CMTE from the closed form to the open one. The fluorescence of C540A was considerably quenched in the presence of CMTE even before photoirradiation for isomerization as is shown in Table 1, although the open form isomer shows no spectral overlap between the absorption of CMTE and the fluorescence of C540A and hence no singlet energy transfer from C540A to CMTE should occur. One possible reason is that since C540A was excited at 435 nm where there is a slight absorption of the open form of CMTE, partial isomerization of CMTE from the open form to closed one could occur, which results in the partial quenching of fluorescence, especially at high CMTE concentrations. This phenomenon can be overcome by selecting a better combination of a photochromic compound and a fluorescent dye so that the fluorescent dye has an excitation wavelength far from the absorption region of the open form isomer.

Another fluorescent dye, PM546, has an absorption peak at 496 nm where the open form of CMTE is transparent, so that the problem mentioned above may be avoided. Changes in fluorescence spectra excited at 496 nm of a PMMA film containing 0.25 wt % of PM546 and 9.97 wt % of CMTE before and after photoirradiation are shown in Figure 2B. Strong peaks around 496 nm are due to scattering of the excitation light. After UV irradiation, the fluorescence of PM546 became completely quenched due to the photoisomerization of CMTE from the open form to the closed one, and by photoirradiation around 500 nm on the film, the fluorescence of PM546 reappeared due to the backward photoisomerization of CMTE from the closed form to open form. The fluorescence of PM546 was also quenched in the presence of CMTE before photoisomerization even though the detection of the fluorescence was carried out with light in a transparent region of the open form isomer, but it was to a much lesser extent compared to the case with C540A. The reversible on−off cycles of the fluorescence could be repeated more than 20 times by alternative irradiation of UV and visible light on the PMMA film. Fluorescence patterning was also obtained with PM546 and CMTE by using a mask.

The fluorescence intensities of the PMMA films with various concentrations of CMTE before, I_b, and after, I_a, photoisomerization are summarized in Table 1. The fluorescence intensity ratio, I_b/I_a, can be a parameter for fluorescence contrast of a system, and the system with larger values of I_b/I_a is regarded as the system with better contrast. The PMMA films containing PM546 have values at least 10 times larger than those containing C540A, and therefore PMMA films containing PM546 have much better fluorescence contrast than those containing C540A.

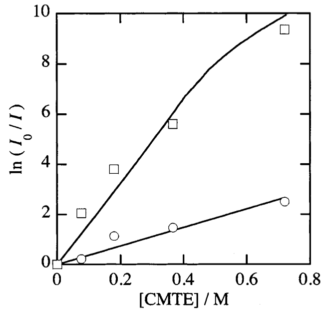

Figure 3. Perrin plots for fluorescence at 550 nm of PM546 (0.25 wt %) in PMMA films containing CMTE before photoisomerization (○) and after photoisomerization (□). Fluorescence excitation wavelength: 496 nm.

As for the mechanism of the present fluorescence quenching, a linear Stern–Volmer plot[16] of the fluorescence of PM546 (lifetime, $\tau_0 = 7.6$ ns) in dichloromethane solution in the presence of several concentrations of closed form of CMTE corresponded to the rate coefficient for quenching, $k_q = 4.7 \times 10^{11}$ L mol^{-1} s^{-1}. This value indicates an efficient excitation energy transfer between PM546 and the closed form of CMTE. The explanation of the present results by an emission–absorption effect or "trivial energy transfer"[16] can be excluded because the "trivial" case requires a large optical density of the acceptor in the system and the optical density of the closed form of CMTE in the present case is about 0.2 or less (Figure 1(B)a).

Energy transfer in a solid film observed in the present experiments is supposed to proceed when there is no molecular diffusion and the Perrin equation (eq 2)[16,17] holds

$$\ln(I_0/I) = C/C_0 \qquad (2)$$

where I_0 and I are the luminescence intensities of donor in the absence and presence of acceptor, respectively, C_0 is the critical concentration of quenching, and C is the concentration of the acceptor. The plots of $\ln(I_0/I)$ vs C in Figure 3 for the PMMA films containing CMTE (acceptor) and PM546 (donor) give the critical concentrations, C_0, for fluorescence quenching of PM546 with CMTE before and after photoisomerization to be 0.27 M (7.25 wt %) and 0.084 M (2.28 wt %), respectively.

In conclusion, we demonstrated the fluorescence switching in a PMMA film containing both a fluorescent dye and a photochromic compound by photoisomerization of the photochromic compound. The high fluorescence contrast and complete on–off of fluorescence in the polymer film have been realized by using PM546 as a fluorescent dye and CMTE as a photochromic compound. The excitation energy transfer between a fluorescent dye and a closed form of CMTE is the mechanism of fluorescence quenching in the present case.

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